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# Towards sewage sludge based biofuels via thermochemical conversion – A review

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ABSTRACT

Wastewater treatment leads to an increase in sewage sludge production. Sewage sludge consists, in general, of non-toxic organic matter and therefore can be utilized as a biomass resource for energy production. Energy recovery from sewage sludge via thermochemical valorization processes seems of great potential. Processes' products can be used as bio-fuels, while minimization of the environmental impacts can be also achieved. In particular, wet sewage sludge pyrolysis-partial gasification at high temperatures and especially gasification give a new perspective for hydrogen-rich fuel gas production. Co-processing of sewage sludge with biomass improves the fuel's characteristics and enhances the processes efficiency. In addition, blends of sewage sludge with biomass contribute in diluting the inorganic and toxic compounds. Towards that direction, algae production using wastewater resources and then to be used for biofuels production seems a sustainable solution that is the reason why exploitation of such a material through thermochemical processes is under intensive discussion.



**Contents**



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## 1. Introduction

On the basis of world and E.U. countries demographic projections [1,2], it is estimated that the amount of sewage sludge derived from municipal waste water treatment facilities will rise. In the mean while, energy demands globally increase. Fossil fuels' price fluctuations and over-consumption in parallel with energy production methods with increased carbon footprint lead to an increase in greenhouse gas (GHG) emissions and consequently on global warming [3]. Identifying alternative renewable sources of fuel and innovative energy production methods, which are potentially carbon neutral, has received increased interest during the latest decades.

In recent years, application of the Directive 91/271/EEC, along with its amendment 98/15/EEC concerning the issue of the management of municipal wastewater, lead to the construction of Waste Water Treatment Plants (WWTP), across the European Union (E.U.) countries, in order to protect the public health and the environment, particularly the receiving water bodies [4]. During the operation of a WWTP, significant amounts of sludge are being produced, but also other by-products, such as screenings and sand. Those by-products in parallel with sludge require safe and environmentally sound management and disposal strategies to prevent the risk of secondary pollution.

Therefore, WWTPs operation addresses a new challenge concerning waste water sustainable management, revealing a new major environmental problem; the management and the long term disposal of sewage sludge, which has so far found only few satisfactory or viable solutions either targeted for energy or high-added value materials production [5,6]. Thus, up to the present most of the sewage sludge produced during municipal effluent treatment has been used in agriculture as a valuable fertilizer, disposed off in landfills or via combustion, incineration and, also as a co-fuel in industry [7]. However, there are several factors restricting these options, such as the accumulation of undesirable substances to sludge (e.g., heavy metals, pathogens and organic pollutants) which potentially pass on to the food-chain [8]. Agricultural use is increasingly regarded as an insecure handling route. The other conventional route of sludge disposal in landfills is held back due to E.U. recent legislation and increased gate costs. Incineration on the other hand provides a large volume reduction of sewage sludge and results in improved thermal efficiency. However, the scrubbing costs of the product gases for air pollution control are usually very high; thus it is important to introduce mature, integrated alternatives for sludge handling and disposal when planning sewage management strategies.

Among the various sludge management options, energy recovery through thermochemical valorization processes seems one of the key alternatives. The principal goal of thermochemical processes is the valorization of sewage sludge energy content, while minimizing the environmental impacts in order to meet the increasingly stringent standards. Although new technology has opened up the potential for sewage treatment and recycling, the investment and operating costs are still high, rendering sludge future management influenced with novel technologies.

The development of thermochemical processes involves global players that serve a global market. However, markets for sewage sludge pyrolysis and gasification are estimated to be influenced on niche applications and government support such as government funding, special incentives for renewable energy investments; therefore the application of those technologies is still confined to the national level.

Countries like Greece facing significant problems concerning the management and disposal of sewage sludge, at the moment stocked in wastewater treatment plants or disposed off to landfills, or even dried still need sustainable solutions. Sludge management from production to end use and by-products exploitation seem already a necessity; compliance of Greece with existing E.U. Directives concerning in situ sludge management and contribution to the European policy and legislation is an issue of great importance of the country.

The aim of this study is to discuss the potential of bio-fuels production from sewage sludge through thermochemical processes and to assess qualitatively these options with respect to their development stage, energy recovery efficiency and expected future improvements. Furthermore, the improvement of the fuel's characteristics by mixing sludge with biomass, the cultivation of algae in sludge and their further exploitation for fuel production with simultaneous sustainable waste management, is also discussed. In this review paper, based on a literature review, an attempt has made in order to approach the issue in an integrated way; in this context, the effect of the presence of moisture and inorganic components in sludge is, also, discussed.

## 2. Regulations determining management choices

National and E.U. legislation usually sets the quality standards of sewage sludge for the different disposal and recycling routes. The institutional framework's agenda defines the terms and restrictions on the sewage sludge management, disposal and recycling routes and alternatives. The E.U. legislation analysis (according to the 1986/278/EEC Directive), and the countries harmonized national legislation shows that the requirements and limitations concerning the sludge utilization focus primarily on its usage in agriculture. At the moment, other uses or disposal methods of sludge fall into more general provisions relating to waste management, which are described in the following Directives [4,7]:

- Directive 1975/442/EEC on waste along with its amendments 1991/156/EEC and 2006/12/EC of the European Parliament and of the Council.
- This directive was supplemented by entries appearing in the subsequent acts of the European Community, namely the so-called "Waste Directive". The Directive firmly established rules for the problem of dealing with sewage sludge.
- Directive 1999/31/EEC on the landfill.
- Directive 2003/33/EEC on establishing criteria and procedures for the acceptance of waste at landfills; pursuant to the Article 16 and Annex II of Directive 1999/31/EC.
- Directive 2000/76/EEC on waste incineration.
- Directive 1989/369/EEC on the prevention of air pollution from municipal waste incineration plants.
- Directive 1991/676/EEC on the water protection from pollution by nitrates from agricultural sources.

- Council Directive 91/689/EEC on hazardous waste.
- Directive 2001/118/EEC about the European Waste Catalogue (EWC).
- Decision 2000/532/EC establishing a list of wastes, as amended.
- Future sewage sludge handling strategies are also influenced by other law enforcements, such as the following [9,10]:
- Kyoto protocol in conjunction with European Union 20-20-20 Renewable Energy Directives targeted at 20% GHG emissions' reduction, from 1990 till 2020, 20% energy consumption decrease and 20% minimum renewable energy ratio increase in the energy mix, by 2020.
- European Union Emissions Trading System (EU ETS) and Climate Change Agreements (CCAs)

## 3. Sewage sludge characteristics

The various sewage treatment systems in conjunction with existing legislation regulate the characteristics and management options of sewage sludge. In addition to the legal framework, ISO and CEN committees establish international standards and set out recommendations on sludge management. In particular, **CEN/TC 308** on characterization of sludge has published or is in progress of producing reports and standards. **TC 308 WI 00308105** standard on characterization of sludge (and other organic wastes) regarding thermal processing (incineration, gasification, pyrolysis and wet oxidation) is under development [11].

Wastewater is processed via physical (sedimentation, floatation), chemical (coagulation, flocculation) and biological methods and individual wastewater treatment procedures are combined into a variety of systems, classified as primary, secondary, and tertiary wastewater treatment in order to reach different levels of removal of the contaminants, meet the stringent legislated limits concerning the purification and hygienization of the water exit stream and facilitate the by-products' management [5,12]. Depending on the stage of the treatment, the following types of sludge are produced:

- *Primary sludge:* Sludge produced during the primary treatment of sewage. Heavy solids are removed via sedimentation by gravitational settling in a quiescent basin while oil, grease and lighter solids float to the surface [6]. The settled and floating materials are removed and the remaining liquid may be discharged or subjected to secondary treatment.
- *Biological sludge*: Sludge produced during the secondary treatment of sewage. During secondary treatment the dissolved and suspended biological matter is removed. Indigenous, waterborne microorganisms, mostly bacteria, are the active agents which typically perform the treatment in a controlled habitat. Secondary treatment may additionally require a separation process to remove the microorganisms from the treated water prior to discharge or tertiary treatment [6,13]. Biological treatment processes are considered the most environmentally and economically compatible of wastewater treatment methods [14]. The microorganisms break down the organic materials present in municipal wastes and thus enabling the valorization of the residues by the production of high added-value compounds such as a diverse range of microbial-derived substances including biopolymers and bio-fuels [15].
- *Mixed sludge*: a mixture of primary and biological sludge.
- *Tertiary sludge*: Sludge produced in the tertiary or advanced wastewater treatment. The treatment is necessary when a high level decontamination is required, for example in the sensitive areas identified in the Member States [7]. The treatment is designed to remove unwanted nutrients mainly nitrogen and phosphorus through high performance bacterial or chemical processes.

**Table 1**
Typical characteristics of sludge – Impact of treatments on the sewage sludge composition and properties [7].

| | A | B1 | B2 | C | D |
|---|---|---|---|---|---|
| Dry matter (DM), g/l | 12 | 9 | 7 | 10 | 30 |
| Volatile matter, % DM | 65 | 67 | 77 | 72 | 50 |
| pH, % VM | 6 | 7 | 7 | 6.5 | 7 |
| C, % VM | 51.5 | 52.5 | 53 | 51 | 49 |
| H, % VM | 7 | 6 | 6.7 | 7.4 | 7.7 |
| O, % VM | 35.5 | 33 | 33 | 33 | 35 |
| N, % VM | 4.5 | 7.5 | 6.3 | 7.1 | 6.2 |
| S, % VM | 1.5 | 1 | 1 | 1.5 | 2.1 |
| C/N, – | 11.4 | 7 | 8.7 | 7.2 | 7.9 |
| P, % DM | 2 | 2 | 2 | 2 | 2 |
| Cl, % DM | 0.8 | 0.8 | 0.8 | 0.8 | 0.8 |
| K, % DM | 0.3 | 0.3 | 0.3 | 0.3 | 0.3 |
| Al, % DM | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 |
| Ca, % DM | 10 | 10 | 10 | 10 | 10 |
| Fe, % DM | 2 | 2 | 2 | 2 | 2 |
| Mg, % DM | 0.6 | 0.6 | 0.6 | 0.6 | 0.6 |
| Fat, % DM | 18 | 8 | 10 | 14 | 10 |
| Protein, % DM | 24 | 36 | 34 | 30 | 18 |
| Fibres, % DM | 16 | 17 | 10 | 13 | 10 |
| Calorific value, kWh/t DM | 4200 | 4100 | 4800 | 4600 | 3000 |

A: primary sludge, primary sludge with physical/chemical treatment or high pollution load1, B1: biological sludge (low load), B2: biological sludge from clarified water (low and middle load), C: mixed sludge (mix of A and B2 types), D: digested sludge.

The sludge produced by WWTPs is usually subjected to an additional treatment to reduce the water content, stabilize the organic matter in the final product and be disinfected; thus it becomes suitable for final disposal and reuse.

The treated sludge is classified mainly into two categories, as follows: aerobic stabilized sludge and anaerobic stabilized sludge. Fig. 1 exhibits a conventional WWTP as well as the points of sludge generation in the treatment process [16]. The structural and chemical composition as well as the behaviour on thermal conditions of sewage sludge highly depends on the pollution load of effluent to be treated, and/or also, on the technical and design features of the waste water treatment process, as well as on the sludge treatment (stabilization technology). Typical characteristics of sludge in relation to the treatment type are presented in Table 1 [7].

The load (Cm) in Table 1 is defined as the ratio between the daily mass of pollution to be removed and the mass of bacteria used for de-pollution. Usually the following levels are defined:

- *high load*: Cm > 0.5 kg $BOD_5$/kg sludge/day
- *middle load*: 0.2 < Cm < 0.5
- *low load*: 0.07 < Cm < 0.2

Sewage sludge produced in municipal wastewater treatment plants is a complex mixture of organic and inorganic materials and contains a wide variety of substances and microorganisms in suspended or dissolved form, which are initially in the liquid phase of wastewater. Some ingredients in the sludge such as non-toxic organic matter (approximately 60% on a dry basis) and nutrients are valuable components. Ingredients with agricultural value are organic matter, nitrogen, phosphorus, potassium and to a lesser extent calcium, sulphur and magnesium while other inorganic components such as silicates, aluminates are also present. In addition, sewage sludge has high calorific value; in dry form has similar calorific value of fossil coals [6]; making it suitable for a wide range of uses.

However, sewage sludge carries undesirable body pollutants such as heavy metals (Zn, Pb, Cu, Cr, Ni, Cd, Hg and As with

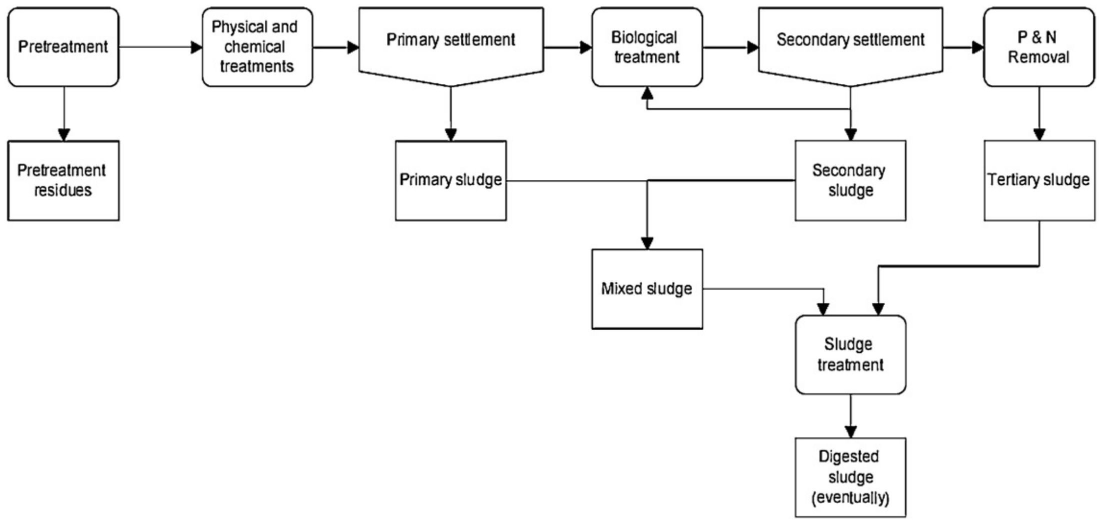


**Fig. 1.** Wastewater treatment and sludge generation [15].

concentrations varying from more than 1000 ppm to less than 1 ppm), synthetic organic compounds (polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), dioxins, pesticides, linear-alkyl-sulphonates, nonyl-phenols, polybrominated fire retardants, etc.) and pathogenic micro-organisms. Thereby, the methods of disposal of that by-product may lead to significant environmental impacts such as public health risks and the possibility of contamination of atmosphere, soil and water resources; thus, appropriate treatment, controlled disposal and careful management are, in general, of great importance [7,13,17].

As far as it concerns the chemical structure of the sludge, it is composed mainly of bacterial constituents (nucleic acids, proteins, carbohydrates and lipids) and their decay products, undigested organic material (cellulose) and inorganic material. Finally, the functional groups of the chemical structure of sludge are aliphatic, carboxylic, amide, amine, aromatic, methylene groups, and even halogens, silicon and phosphorous [18].

The sludge produced in WWTPs has high moisture content, normally, even more than 95 wt%. The water content of sludge is divided into the following categories [19,20]: (a) free moisture content which can largely be removed by mechanical (thickening and compression) means, (b) capillary moisture which can be removed by thermal drying, (c) particle's surface moisture that refers to water molecules adsorbed on the surface of the solid and also removed by thermal drying and (d) chemically bonded water molecules with the solid that does not respond during drying.

Prior to sludge supplying in drying provisions, aggregation of the solids is required adding an appropriate quantity of flocculants (lime, organic polyelectrolyte, salts of trivalent Al or Fe) [19]; thus, those chemicals influence sewage sludge characteristics.

## 4. Thermochemical conversion of sewage sludge

During the last decades, the thermochemical processes are considered one of the most promising ways in order to produce energy and valuable products from waste residues. Sewage sludge produced in WWTPs could be considered, in its dry form, as a special case of biomass due to the increased quantity of organic and high enough calorific value. Sludge contains high humidity and much of the energy content of the dry solids is consumed for drying. Despite this, the thermochemical, sewage sludge conversion, processes are energy self-sufficient, while the most important issues relate to their energy efficiency, moisture exploitation for hydrogen rich fuel gas production, niche and expensive antipollution gas equipment [21,22].

### 4.1. Pyrolysis

Pyrolysis is the process of thermal degradation of fuels' chemical molecules in an inert atmosphere. The temperature range, in which, pyrolysis takes place, varies from 300 °C to 900 °C and results in sewage sludge's conversion into fixed carbon, ash, bio-oils, combustible gases and also water vapours [23]. Pyrolysis is environmentally friendly, compared to the widespread application of combustion and incineration, in terms of clean gas emissions [24].

In general, pyrolysis of organic materials such as lignocellulosic, plastics, and municipal solid wastes has received renewed attention due to the possibility of converting these wastes into useful energy or into valuable chemicals while fewer studies are published on sludge pyrolysis. Pyrolysis of sewage sludge has attracted much attention as an economically and environmentally acceptable method for the beneficial utilization of sewage sludge in recent years [25–28]. Moreover, pyrolysis of sewage sludge presents the advantage of concentrating the heavy metals (except mercury and cadmium) present in the final residue [29–31]. The lixiviation of these metals is minor in the case of the ashes of pyrolysis in contrast to the ashes of incineration [29,31,32]. In this way, its final disposal in landfills is most secure.

Several modifications of the pyrolysis process exist, dependent on each operation equipment and conditions. Several studies have been carried out on fixed or fluidized bed, circulating, pyrolysis using a rotary reactor, microwave and electrical furnaces pyrolysis, and flash, fast or low heating rate pyrolysis using dry or wet sludge as feedstock [24,31,33–36].

#### 4.1.1. Pyrolysis products

The products of the pyrolysis process can be classified into the following fractions: (a) stable (non-condensable) *gases*, mainly, consisting of hydrogen, carbon monoxide, carbon dioxide, methane and in small concentrations contains low molecular weight hydrocarbons, (b) *liquids* (tar and/or oil), particularly hydrocarbons, organic acids and carbonyl compounds of high molecular weight phenols, aromatic compounds, aliphatic alcohols, acetic acid and water and (c) *solid*, mostly solid carbon and ash (with significant amount of heavy metals) the rate of which during the pyrolysis of sewage sludge is significantly [23,33].

**Table 2**
Heating values of some conventional and unconventional solid, liquid and gaseous fuels [38].

| Fuels | Heating value |
|---|---|
| Coal | 14,600–26,700 kJ kg$^{-1}$ |
| Plastics, wood, paper, rags, garbage | 17,600–20,000 kJ kg$^{-1}$ |
| Wood | 16,000–20,000 kJ kg$^{-1}$ |
| Dry sewage sludge | 12,000–20,000 kJ kg$^{-1}$ |
| Wet sewage sludge | 1000–3000 kJ kg$^{-1}$ |
| Gas-oil | 45,500 kJ kg$^{-1}$ |
| Black liquor | 12,500–15,500 kJ kg$^{-1}$ |
| Natural gas | 38,000 kJ kg$^{-3}$ |
| Coke-oven gas | 19,000–22,000 kJ kg$^{-3}$ |
| Synthetic coal gas | 10,800 kJ kg$^{-3}$ |
| Blast-furnace gas | 4400–5300 kJ kg$^{-3}$ |

All the three above-mentioned groups of products can be used as bio-fuels. The organic fraction of the pyrolysis liquids, which does not include aqueous fraction with hydrosoluble organic compounds, being 30–40% of the total liquid fraction shows the highest heating value among all the pyrolysis products. The heating value ranges between 22,400 and 28,000 kJ kg$^{-1}$ (dry basis) [37] and is comparable to some conventional fuels and even higher than that of other waste-residues commonly used as fuels as shown in Table 2 [38]. The potential utilization of these liquids for energy production purposes either in their natural form or transformed after further processing into other more convenient fuels cannot be ignored. The perceived ability of the latter towards the direction of replacing liquid fossil fuels in internal combustion engines focuses the research on maximizing the production of pyrolysis liquid products (bio-oil, bio-crude oil) [33,36,39,40]. However, the design complexity and relative infancy of the technology makes it currently unsuitable for stationary-constant power applications. In addition, the gas fraction represents a significant proportion of the pyrolysis products with heating value comparable to those of some fuels gases, ranging between 12,000 and 20,000 kJ/m$^{-3}$ [37], depending on the process conditions [38]. An optimization of the pyrolysis process would yield gases that could be used to enhance the energy balance of the process and even place emphasis on the maximization of the bio-gas product.

*4.1.1.1. Liquid products.* Tar resulting from pyrolysis of dry sewage sludge is an unknown and complex mixture which contains hundreds of organic compounds that belong to a wide variety of chemical groups [41–43]. Pyrolysis oil can be analysed through GC–MS analysis. Molecular distribution and structure (H NMR) can be investigated. In general, the liquid product of pyrolysis consists of a group of aromatic clusters connected by long straight chain hydrocarbons with hydroxyl groups. Optimum utilization of the oil, as a bio-fuel, is achieved when straight chain hydrocarbons exist, since their main characteristics are the high heating value and the low viscosity [39].

Tar is a sub product of pyrolysis present in the liquid product. Many studies have been performed in order to assess the tar composition produced by sludge pyrolysis varying several parameters of the process. Kaminsky and Kummer [34] pyrolysed sludge in a fluidized bed type reactor, focusing on the diverse composition of the oil fraction by varying temperature. Dominguez et al. [44], performed FTIR and GC–MS analyses to characterize the oil produced by sewage sludge pyrolysis in a conventional and a microwave induced heating, indicating that the oil produced from conventional heating contained a high proportion of aromatic hydrocarbons comparing to microwave heating. Konar et al. [45] on the other side carried out pyrolysis over activated alumina as catalyst, reducing in that way the quantity of carbonyl groups in the liquid product. Fullana et al. [46,47] showed that nitrogenated compounds were typically present in sewage sludge oils and could be divided into five different groups (nitriles, pyridines, amides, amines and polyaromatic nitrogenated (PAN) compounds). Furthermore, the large amount of nitrogenated and oxygenated hydrocarbons, and especially amide and nitrile compounds in sewage sludge pyrolysis oil was also reported by Tsai et al. [48].

On the other hand, wet sewage sludge in depth pyrolysis studies [49] revealed that tar contained mainly large amounts of multiplicate aromatic hydrocarbons (up to six rings) and a few aliphatics, being consistent with the above-mentioned scientific works. The main components identified by Zhang et al. [49] in the tar from sludge pyrolysis have been classified into 6 groups: 1-alkenes, monoaromatic hydrocarbons and their respective alkyl derivatives, with the dominant compounds to be polycyclic aromatic hydrocarbons (PAHs), substituted aromatics containing N, S, Cl and O, and aromatic nitriles. Besides heavy oxygenated hydrocarbons such as carboxylic acids, ketones and esters, halogenated aromatics, alkyl aromatic hydrocarbons and cyclanes were also detected in tar from sludge pyrolysis.

Tian et al. [50] report the N and S content in the bio-oil and mark the need for extraction in order to be used as fuel.

*4.1.1.2. Gaseous products.* As far as it concerns the gaseous fraction, Conesa et al. [51] studied the evolution of gases in the primary and secondary pyrolysis of different sewage sludge digested both anaerobically or aerobically. They indicated that the primary pyrolysis of sewage sludge produces a high quantity of chemicals (45 wt%), which are principally hydrogen, water, hydrocarbons (C1–C4), methanol, chloromethane, carbon dioxide and acetic acid. Many studies [24,36,37,45,49,52,53] confirm that $H_2$, CO, $CO_2$, $CH_4$ and some light hydrocarbons ($C_2H_2$, $C_2H_4$, $C_2H_6$ and $C_3H_8$) are the main components ($N_2$ free-vol%) released during sewage sludge pyrolysis. Bellmann et al. [29] pyrolysed sludge in a fluidized bed reactor and obtained a gas fraction of 40 wt% at 750 °C. Kasakura and Hiraoka [54] sludge pyrolysis study experiments in a pilot plant, resulted in gas constituents yields of $H_2$ (5.5 vol%), CO (3.65 vol%), methane (1.48 vol%), and other light hydrocarbons in lower concentrations, while other products of interest identified were HCN, nitrogen oxides, hydrogen chloride and sulphur oxides. Extensive reference on N-, S- and Cl-compounds at the gaseous fraction is being made below.

*4.1.1.3. Solid products.* The solid product is a carbonaceous material known as pyrolytic char. There is an obvious relationship between the chemical structure of solid char and the composition of other fractions. Solid carbonaceous residues' relatively low heating value in comparison to that of other fuels, along with high concentration of heavy metals renders the char unsuitable for further exploitation of its energy content [55]. The char resulting from pyrolysis of sewage sludge is more resistant to lixiviation than that of raw sludge or ashes produced by combustion or incineration [32,56]. The structural characterization of the sludge pyrolysis carbons are commonly performed by physical absorption of $N_2$. The char appears to have low surface area maybe due to its high ash content, making it suitable for landfilling according to Karayildirim et al. [57]. Using the char as absorbent preferable to acidic compounds such as $SO_2$ or $SH_2$ and other pollutants like phenols and phenol-derives is another disposal possibility [58], compatible with the previous mentioned option of landfilling.

Lu et al. [59] studied surface area and pore structure development at the resultant chars during pyrolysis of sewage sludge; thus, the surface area of the resultant char increases with temperature and hold time, however, loss of volatiles in the intermediate thermoplastic phase leads to pore enlargement and surface area reduction of the chars obtained at 550–650 °C. Due to sintering, high temperatures and prolonged times also reduce meso-pore

**Table 3**
Substance decomposition temperature range [40].

| Compounds | Temperature range (°C) |
|---|---|
| Moisture | Up to 150 |
| Carboxylic | 150–600 |
| Phenolic | 300–600 |
| Ether oxygen | Up to 600 |
| Cellulosic | Up to 650 |
| Oxygen containing compounds | 150–900 |

volume. The optimum process parameters were found to be 850 °C and 2 h.

Most of the porosity of the solid residue is due to macropores, while the meso- and micro-pore volumes are relatively low [37,59–61].

*4.1.2. Parameters affecting products' yields*

The factors that basically determine the relative proportion and yields of the three pyrolysis products are (a) process temperature, (b) residence time of the feedstock and the processes' intermediate products in the reactor, but also (c) pressure, (d) turbulence and (e) the raw materials' characteristics [21]. More specifically, sludge product yields obtained from the pyrolysis process are determined by the raw material decomposition (primary) reactions and the intermediate reactions with the primary volatiles (secondary reactions) [51]. The extent of the secondary reactions depends on the experimental unit as well as the operating conditions. It is well known that high residence times and high temperatures favour the secondary reactions.

Based on the literature review that follows, it is estimated that low temperatures (∼300 °C) and high residence times lead to carbonization (up to 90 wt% of the original organic solids), high temperatures (∼900 °C) and high residence time lead to increased gas yield (up to 90 wt% of the original organic solids), while maximization of liquid products (up to 70 wt% of the original organic solids) occurs in average temperatures (∼500 °C) and very fast process.

According to process temperature pyrolysis is classified into gasification and liquefaction type. Pyrolysis–gasification (above 650 °C) mainly produces bio-gas yielding between the range from 51 to 66 wt.% of dry sewage sludge [62] while pyrolysis–liquefaction (around 425–575 °C) leads to 30–40 wt.% bio-oil production [63].

Numerous researchers have been studied the maximization of the gases, tars and chars, depending on the specific interest by the effect of pyrolysis conditions (such as temperature and heating rate) on the pyrolysis of sewage sludge [24,37,52]. Shen and Zhang [33] in low-temperature pyrolysis experiments in a fluidized bed reactor showed that carboxylic and phenolic compounds of the original sludge seemed responsible for the pyrolysis oil production. The statement was based on an extensive literature concerning the various temperatures where chemical substances decompose, as Table 3 indicates [40]. The maximum oil yield was achieved at 525 °C, that belongs to the temperature range in which carboxylic and phenolic groups decompose enforcing the conclusion that these compounds are mainly responsible for the pyrolysis oil production.

The study on low-temperature pyrolysis in a fluidized bed reactor [33] report that the maximum oil yield (30%) was achieved at 525 °C and with residence time 1.5 s, while, flash pyrolysis of a mixture of raw and activated sludge, for 0.55 s, using the same type of reactor, indicated that maximum liquid yield of 52% was obtained at 450 °C [36].

As far as it concerns the way of heating, it is stated that microwave treatment of raw wet sewage sludge results to drying. However, at high temperature, in the range of 900 °C, pyrolysis rather than drying occurs when the raw wet sewage sludge is mixed with pyrolysis char, which is a microwave receptor [24]. Compared to conventional heating in electrical furnaces or fluidized bed reactors, microwave treatment is more efficient and saves time and energy (power), for the same level of pyrolysis. According to Zhang et al. [49], in the case of pyrolysis at different temperatures of sewage sludge with high moisture content of 84 wt%, a significant increase in gas yield above the temperature of 700 °C was observed reaching its maximum value (36 wt%) at 1000 °C. The feasibility of producing hydrogen – rich fuel gas from pyrolysis-partial gasification of wet sewage sludge was studied by Xiong et al. [64], and led to an increase in the gas production and the yield of hydrogen. Chu et al. [65] added a flocculent in raw sewage sludge in an attempt to improve the sludge dewaterability; an impact in the pyrolysis process was observed. Specifically, at high heating rates the flocculent enhanced the pyrolysis rate.

Another important parameter in sludge conversion is the effect of sewage sludge characteristics issued from anaerobic wastewater treatment on the thermochemical processes' efficiency. Organic compounds of sewage sludge, issued from anaerobic digestion, decompose at higher temperatures affecting in that way its thermochemical treatment. Anaerobic digestion leads to the production of more complicated structure of the organic compounds in sewage sludge more complicated, but the overall composition of sludge is less simplified [66].

Therefore, according to Conesa et al. [51] dried sewage sludge pyrolysis was concluded that two main differences between anaerobic and aerobic sludge appear: acetic acid production during aerobic treatment is much higher than during anaerobic treatment and in anaerobic digestion, the initial production of acetic acid, by acetogenesis, is continued by methanegenesis, producing a series of highly degraded compounds. On the other hand, in the aerobic digestion, the bacteria responsible for the methanegenesis are absent and many of the remaining compounds contribute to the production of acetic acid.

An also remarkable feature is that biodegraded organic matter in aerobic process, responsible for the production of a series of highly degraded, easily volatilized compounds that comparatively produce lower pyrolysis char yield. Moreover, Domínguez et al. [53] verifies that the distribution of the pyrolysis process products and the composition of the gaseous fraction depend to a large extent on the nature of the raw material. Fonts et al. [18] studied the pyrolysis of anaerobically digested sewage sludge originating from three different urban WWTPs and found that the pyrolysis product distribution and characteristics highly depend on the volatile and ash content of sewage sludge.

*4.1.3. Parameters affecting products quality*

It is known that the pyrolysis temperature has a significant effect on the composition of the different fractions. As far as it concerns tar composition several studies [41–43] indicate that the amounts of PAHs were negligible when the pyrolysis temperature was below 500 °C and an important increase in their yields took place for temperature above 700 °C, indicating that high temperatures give rise to a toxic tar rich in PAHs.

The same previously mentioned group of researchers [49] indicated that the concentrations of 1-alkenes in tar decreased with temperature. It can be observed that the relative content of 2-ring polycyclic aromatic hydrocarbons (PAHs) increased dramatically from 17% to 27.4% as the pyrolysis temperature increased from 600 to 1000 °C, while the mono-aromatic hydrocarbons showed a significant reduction. Meanwhile, 3–4 rings PAHs increased sharply from 600 to 800 °C, followed by slower growth between 800 and 1000 °C. Moreover, the content and species of higher ring PAHs increased slightly as the temperature increased, while formation and growth of PAHs was accompanied by the release of $H_2$.

On the other hand gas composition at different temperatures, showed that $H_2$ and CO content significantly increased with temperature increase above 650 °C [24,37,52,53]. $H_2$ in the case of wet sewage sludge pyrolysis, increased almost linearly from 14 to 31.6 vol% as the pyrolysis temperature increased from 600 °C to 1000 °C, while the CO gas content increased significantly from 25.5 to 34.8 vol %. The concentration of CO + $H_2$ (vol%) and $H_2$/CO ratio (v/v) reached their maximum value (66.4 vol% and 0.91) at 1000 °C, respectively, opposed to the contents of $CO_2$ and $CH_4$ that decreased gradually with temperature [49,53]. Dry sewage sludge pyrolysis [37] shows in general, the same tendency with temperature. $H_2$ and CO concentrations in the gas fraction are higher compared to those resulting from wet sewage sludge pyrolysis, however, wet sewage sludge pyrolysis yields higher gaseous product. The abovementioned comparison is indicative to the effect of moisture to the bio-gas composition and process efficiency.

#### 4.1.4. Kinetics

Sewage sludge pyrolysis under different conditions aims at investigating the pyrolysis mechanism. Thermogravimetric analysis (TGA) provides pyrolysis kinetic data in order to improve the insight in the thermal degradation of sewage sludge and classify the material's main components, while obtaining sets of kinetic parameters useful to optimize reactors used in sludge pyrolysis and gasification [67–69]. It has been established that thermogravimetry/mass spectrometry (TG/MS) is a well suitable for the characterization of gaseous thermal degradation products of different waste materials [51,70].

Compared to flash pyrolysis (heating rates > 1000 °C/s), TGA applies low heating rates, in the range of 1–200 °C/min, while permits the monitoring of evolution profiles of products as a function of temperature [71]. Therefore, thermogravimetry, widely used to study the thermal decomposition of polymers and other materials, is one of the techniques used to study the primary reactions of the thermal decomposition of solids. The interpretation of the experimental data can provide information on the composition of the material, order of reaction, number of different processes that take place in the reaction, and the corresponding kinetic constants [51].

Sewage sludge pyrolysis has been explained using several models. Urban and Antal [68] developed a model to predict the weight loss during pyrolysis in a fluidized bed reactor, suggesting two independent reactions associated with the decomposition of dead bacteria and organic matter.

According to Conesa et al. [51,69,72], pyrolysis of sewage sludge can be explained assuming three independent stages, corresponding to biodegradable organic matter, dead bacteria and non-biodegradable compounds which by decomposing form volatiles and char. The most char-forming fraction has been assigned to non-biodegradable compounds, while the other two correspond to biodegradable organic matter and dead bacteria. The model described anaerobically digested and non-digested sewage sludge pyrolysis [72]. Working in the same field Conesa et al. [51] validated their proposed model using data from pyrolysis of anaerobically and aerobically digested sludge, indicating the presence of three stages of decomposition (at 250 °C, 350 °C and 550 °C). In the first, the main products evolved are methane, carbon dioxide, water and acetic acid; in the second, hydrocarbons and alcohols; the third process produces mainly hydrogen, methane, carbon dioxide, hydrocarbons and alcohols. Chloromethane is the unique compound that is produced during the three stages, while water evolution takes place over a wide temperature range. Font et al. [73] assumed fractions of biodegradable organic matter, dead bacteria and non-biodegradable compounds and relate the biodegradable materials with hemicelluloses and the non-biodegradable matter with polymers.

However, only a few studies have been focused on the pathway of the formation of pyrolysis products and the related mechanisms due to the complex reactions taking part among organic matter, non-biodegradable fractions and dead bacteria [32,48,51,68,72]. Shao et al. [66] used a TGA-FTIR technique to investigate the pyrolysis mechanism of sewage sludge by dividing the pyrolysis process into five temperature regions, in which occurs dehydration, intermediates' formation and decomposition and finally char generation. Differential thermogravimetric curves (DTG) provide a means to differentiate between biodegradable and non-biodegradable matter. It is possible to distinguish two, primary and secondary, degradation between 200 °C and 550 °C, which affect biodegradable and non-biodegradable organic matter. Yu et al. [74] divided pyrolysis process into high, medium and low temperature regions, based on an assumption of wet sludge being comprised water, degradable compounds and char.

Sewage sludge is highly heterogeneous and comprises a mixture of various organic and inorganic compounds. Therefore, there are models that assume a large number of components [74]. However, from a thermal point of view, rather than chemical composition, it is important to classify sludge fractions according to temperature response; towards that direction, there are models that assume a low number of components that degrade following parallel reactions [73,75]. In all cases the overall pyrolysis behaviour is the combination of the behaviour of the individual components [76]. The calculated differential thermogravimetric (DTG) curve can be represented by a sum of the individual parent components' behaviour. Number of partial reactions can be varied depending upon the typical number of components proposed for the study. Barneto et al. [77] and Thipkhunthod et al. [75] suggest models with few fractions, taking into account realistic components, to gain insights in the thermal degradation of sludge. In particular, Thipkhunthod et al. [75] proposed a model to relate the presence of dead bacteria in sludge with four components, identified, as hemicellulose, cellulose and lignin, commonly present in lignocellulosic materials, and finally lipid waxes, oils, etc. Carbohydrate and fat present in inner cells may be classified, according to these authors, into cellulose and oil–lipid fractions, with proteins from bacteria to decompose in a temperature range of 300–400 °C similar to cellulosic materials.

Barneto et al. [77], taking into consideration the latter work, simulated the pyrolysis of sewage sludge based in biomass components (low stability organic compounds, hemicelluloses, cellulose, lignin-plastic and inorganic compounds) and concluded that the thermal and kinetic behaviours of the main components of the sludge are similar to those reported for hemicelluloses, cellulose and lignin present in lignocellulosic biomass. The assumption of plastic compounds in sludge content, which degrade in the temperature range of lignin [73], seems reasonable, considering the characteristics of waste products of an urban area [78]. Mass loss related to inorganic matter present in sludge is explained with carbonates [77]. Most of the biodegradable matter is volatized between 150 °C and 400 °C, while non-biodegradable organic matter between 400 °C to 550 °C. Oxygen presence increases the mass loss rate at any temperature.

#### 4.1.5. Pyrolysis mechanism

According to Khiari et al. [21] pyrolysis begins with the vapourization of volatile materials, primary decomposition of non-volatile components follows, producing char, but also tar and gases, while secondary pyrolysis of char, at higher temperature, results in hydrocarbons and aromatic compounds in the volatile phase. A schematic presentation of sewage sludge pyrolysis mechanism is given in Fig. 2 [66].

Hydrogen rich fuel gas production at high temperatures is due to the decarbonylation of oxygenated hydrocarbons and dehydrogenation reactions, intensified as temperature increases, leading

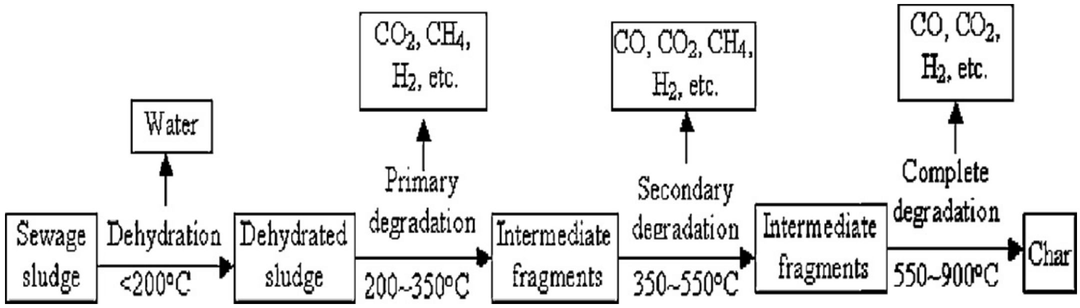


**Fig. 2.** Schematic presentation of pyrolysis mechanism [66].

to an increase in $H_2$ that was released from heavy hydrocarbon compounds. Those reactions predominate over the cracking reactions that give rise to polymerization and polycondensation [37,49]. Additionally, $H_2$ can be considered as a good indicator for secondary cracking of tars [42].

According to Menéndez et al. [24] the breaking of carbonyl and carboxyl functional groups of sludge is mainly responsible for the release of CO and $CO_2$ at temperatures lower than 450 °C. CO is the major secondary product from tar cracking, favoured by high temperatures.

Furthermore, $C_2H_4$, $C_2H_6$ and $C_3H_8$ are also reduced at high temperatures, as the following reactions indicate [79]:

$$C_2H_6 \rightarrow C_2H_4 + H_2$$

$$C_2H_4 \rightarrow CH_4 + C$$

The primary analysis of tar suggests that the decomposition of aliphatics, the breaking of peptide bond in proteins contained in the microbial organisms hosted in the original sludge and the group transfer reactions, such as esterification of aliphatic acids and amidation constitute the main mechanism of sewage sludge pyrolysis [48,49]; thus, sewage sludge pyrolysis oil presents large amount of nitrogenated and oxygenated hydrocarbons, and especially amide and nitrile compounds. According to Morf et al. [42], phenolics are considered to be important precursors for the formation of PAHs. In particular, the parent phenol was identified as a unique precursor for the formation of naphthalene.

Although there are several reaction pathways to explain the formation of PAHs, many researchers [42,43,80], have preferred the Diels–Alder reaction mechanism; this also corresponds well with the relative increase in $H_2$ production as primarily dehydrogenation of alkanes to alkenes/dienes occurs.

Nevertheless, the mechanism of pyrolysis is still not fully understood, especially in the case of wet sewage sludge. Experimental studies of wet sewage sludge pyrolysis report the following [49,53,64]: high moisture content of sewage sludge generates a steam-rich atmosphere at high temperatures, giving rise to the endothermic reactions between the steam and pyrolysis products, which conduces to increase in $H_2$ generation [49].

The main reactions occurred during pyrolysis are as follows [26–28]:

$$C + 2H_2O \rightarrow 2H_2 + CO_2 \quad \Delta H = +75\,\text{kJ/mol} \tag{1}$$

$$C + H_2O \rightarrow H_2 + CO \quad \Delta H = +131\,\text{kJ/mol} \tag{2}$$

$$CH_4 + 2H_2O \rightarrow 4H_2 + CO_2 \quad \Delta H = +165\,\text{kJ/mol} \tag{3}$$

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad \Delta H = +206\,\text{kJ/mol} \tag{4}$$

Some steam partly condenses into liquid fraction, while the rest takes part in the water gas shift reaction and the steam reforming reactions which also contributed to the production of $H_2$ [53,64].

Finally, the formation of gas fraction is a consequence mainly of secondary tar cracking which is intensified at high temperatures, the decomposition of solid char that is attributed to the devolatilization of the hydrocarbons and the partial gasification of the carbonaceous residues in the char at high temperatures and the reactions between the intermediate products formed during pyrolysis [41,44,53,64].

### 4.2. *Gasification*

Gasification is the thermochemical process through which carbonaceous content of the fuel is converted to combustible gas and ash in a net reducing atmosphere. The optimum target is the production of clean combustible gas at high efficiency [23]. The process reduces sewage sludge's volume and puts it into a form suitable for disposal. Gasification is an attractive alternative compared with the predominant applied technology of incineration. Gasification is a net chemically reductive process and thus can circumvent problems commonly encountered with incineration, including the need for supplemental fuel, emissions of sulphur oxides, nitrogen oxides, heavy metals and fly ash, and the potential production of chlorinated dibenzodioxins and dibenzofurans [81].

#### 4.2.1. *The process*

Gasification includes a series of sequential and concurrent chemical and thermal sub-processes. Sewage sludge undergoes physical and chemical changes. The total process is actually energetically self-sustaining at steady-state conditions. The principle stages during gasification are drying, pyrolysis, oxidation and reduction [82]. Specifically, sewage sludge drying takes place within the process as descending to the pyrolysis zone, between the temperature range 70–200 °C. The required heat comes from the partial oxidation reactions. Pyrolysis/thermal degradation of the dried sewage sludge occurs at temperatures between 350 and 500 °C. As a consequence, char, fly ash, water vapours and a complex mixture of condensable, high molecular weight organic compounds and non-condensable stable gases such as CO, $CO_2$, $H_2$ and hydrocarbons of low molecular weight are formed. The necessary heat also comes from the partial oxidation of the pyrolysis products. Finally, pyrolysis' products, condensable and non-condensable vapours and char undergo gasification, where they are concurrently partially oxidized and then reduced to permanent gases at the reduction zone.

The oxidation reactions are highly exothermic, causing a great increase in the temperature (up to 1100 °C); thus, maintaining the endothermic stages of the supply are drying (in the entry area of the gasifier), pyrolysis and gases reforming (in the exit of the gasifier). The oxidation of the condensable organic fraction leads to low-molecular weight products formation and as a consequence reduces the tar in the output. The gas products are reformed to hydrogen and carbon monoxide [82]. Reactions in the zones of oxidation and reduction are as follows [83]:

**Table 4**
Typical product-gas characteristics regarding different agents [85].

| Reactor type | Gas composition (vol% dry) | | | | | Calorific value ($MJ/m^3$) | Gas quality | |
|---|---|---|---|---|---|---|---|---|
| | $H_2$ | CO | $CO_2$ | $CH_4$ | $N_2$ | | Tar | Dust |
| Fluidized bed, air-blown | 9 | 14 | 20 | 7 | 50 | 5.4 | Fair | Poor |
| Updraft, air-blown | 11 | 24 | 9 | 3 | 53 | 5.5 | Poor | Good |
| Downdrafr, air-blown | 17 | 21 | 13 | 1 | 48 | 5.7 | Good | Fair |
| Downdraft, oxygen- blown | 32 | 48 | 15 | 2 | 3 | 10.4 | Good | Good |
| Pyrolysis reactor | 40 | 20 | 18 | 21 | 1 | 13.3 | Poor | Good |

*Oxidation zone*

$$C + O_2 \rightarrow CO_2, \quad \Delta H = -406\,\text{kJ/mol} \tag{5}$$

$$2C + O_2 \rightarrow 2CO, \quad \Delta H = -123\,\text{kJ/mol} \tag{6}$$

*Reduction zone*

$$C + CO_2 \rightarrow 2CO, \quad \Delta H = 162\,\text{kJ/mol} \tag{7}$$

$$C + H_2O \rightarrow CO + H_2, \quad \Delta H = 119\,\text{kJ/mol} \tag{8}$$

$$C + 2H_2O \rightarrow CO_2 + 2H_2, \quad \Delta H = 75\,\text{kJ/mol} \tag{9}$$

$$C + 2H_2 \rightarrow CH_4, \quad \Delta H = -87\,\text{kJ/mol} \tag{10}$$

$$CO + H_2O \rightarrow CO_2 + H_2, \quad \Delta H = -42\,\text{kJ/mol} \tag{11}$$

$$2C + 2H_2O \rightarrow CO_2 + CH_4, \quad \Delta H = -11\,\text{kJ/mol} \tag{12}$$

Reforming includes reactions between hydrocarbons and water vapours, resulting in hydrogen production [84].

$$CxHy + xH_2O \rightarrow xCO + (x + y/2)H_2 \tag{13}$$

Additional hydrogen is produced through the water gas shift reaction

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{14}$$

### 4.2.2. Parameters affecting products yield

Typical reactors operate during gasification of sewage sludge between the temperature range of 800–1400 °C and lead to an average product distribution based on the literature review up to 90 wt% gas, 30 wt% char and 5 wt% tar.

Various gasification reactors types exist, among which, the fixed and fluidized bed are the most widely used. Furthermore fixed bed can be classified to downdraft, updraft and cross-current reactor. Among them, fluidized bed configuration presents higher gasification efficiency, compared to fixed bed gasifiers [85], since enhances mass and heat transfer phenomena; however, the product gas appears to have increased content in tar and solid particulates. In the case of fixed bed reactors, downdraft reactors are proposed to be mostly suitable for the discussed alternative fuel of high moisture content, which requires treatment in combination with heat and power production [82]. High char conversion, low ash carry over, lower tar level, quick response to loading different wastes and simple construction are some of the particular gasifier's advantages explaining the above statement [85].

Gasification medium is an important parameter influencing the gaseous product quality and quantity. Table 4 shows typical product gas characteristics relatively to process type and agent used [85]. Instead of air, steam can be also added as gasification medium, enhancing hydrogen production. Product gas calorific value is dependent on the diluting effect of the gasification medium; between air and steam gasification, air gasification gives gaseous product with the lowest calorific value (nitrogen content ~50%).

Fuel properties such as surface, size, shape, moisture content, volatile matter and carbon content are factors that affect the overall gasification process [86]. Additionally, the drying rate of the feedstock depends on many factors such as fuel surface, recycling rate, and the produced gases' relative humidity, the temperature difference between the supply and the hot produced gases and the internal diffusivity of moisture within the fuel. Pyrolysis as a precursor of gasification obviously determines the latter's results; thus, the above analysis concerning parameters that influence pyrolysis process are taken into account in gasification process design. Fig. 3 schematically presents the pyrolysis–gasification sequence [85].

Raw material composition is also in that case considered. In particular, special reference is being made to the research work of Xie et al. [83] concerning sewage sludge air gasification; sludge emerging from anaerobic digestion shows increased content of CO, $CH_4$, $H_2$ and $C_mH_n$ in the gas fraction, while leads to the production of lower $LHV_{gas}$. On the other hand, the anaerobic process in wastewater secondary treatment from WWTPs can improve the gas quality.

### 4.2.3. Gasification products

The main gasification product is the producer gas and less important char that is either led for combustion or landfilling. Gasification of sewage sludge generates a high-quality combustible gas that can be further burned for power generation and to produce heat for sludge drying [87]. Fundamental research is important in attempt to obtain a desirable gas for electricity production. Furthermore, combustion of the gas product enables destruction of any organic by-products of gasification prior to release to the atmosphere; gasification process enables facile destruction of refractory organic compounds, such as chlorobenzene and polychlorinated biphenyls (PCBs) to 99.9999% destruction removal efficiency (DRE) [81].

Typical combustible producer gas composition includes gas constituents at percentages as it is shown in Table 5 [23]. Gasification gas (producer gas/synthesis gas) can be used either in internal or external combustion engines or in solid oxide fuel cell (SOFC) application for electricity production. The high calorific value of high hydrocarbons present in the gas phase renders the gas suitable to be burnt. However, gas utilization in fuel cells or for $H_2$ production demands reduction of its hydrocarbon contents, char and tar and at the same time maximization of gas yields in $H_2$; therefore, increased process temperature (900 °C), high air flow rates, and even catalysts presence are required [88].

High cycle efficiency of gas turbines in conjunction with gasification makes them attractive in order to convert the energy carried in the bio-fuel to electricity. However, gas engines are more appropriate for smaller size plants. SOFCs give high electrical efficiency,

**Table 5**
Typical combustible gas composition from gasification (vol%) [23].

| Gas constituents | vol% |
|---|---|
| Carbon monoxide, CO | 6.28–10.77 |
| Hydrogen, $H_2$ | 8.89–11.17 |
| Methane, $CH_4$ | 1.26–2.09 |
| $C_2H_6$ | 0.15–0.27 |
| $C_2H_2$ | 0.62–0.95 |

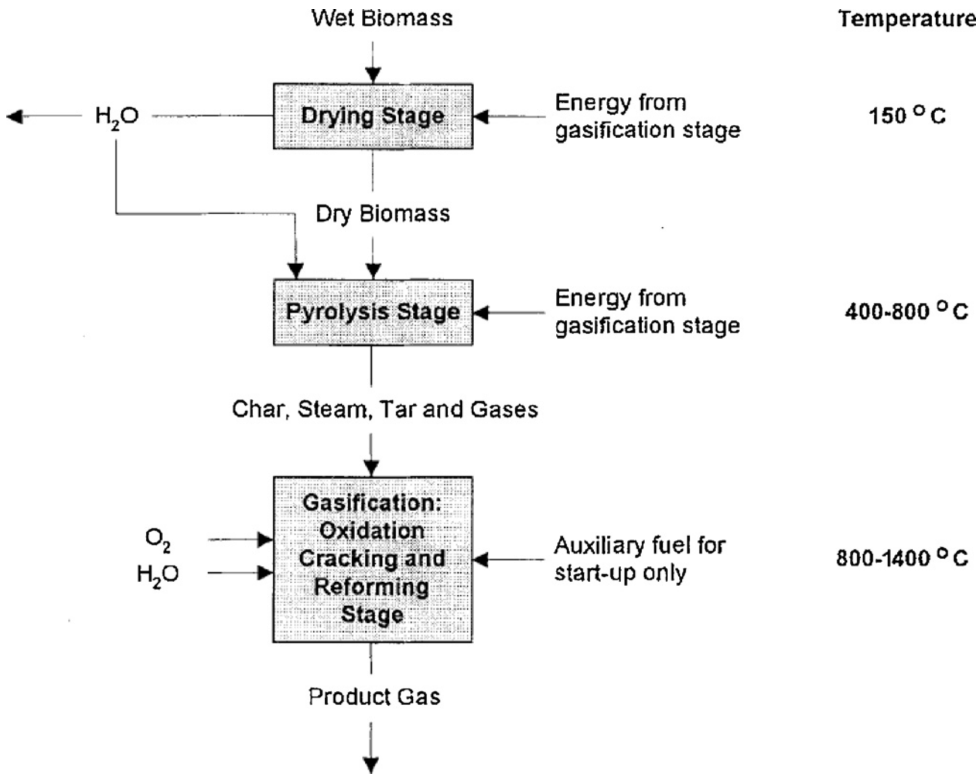


**Fig. 3.** Stages in thermochemical processing [85].

but it is of higher cost compared with the combustion engines; this fact renders their choice economically compatible for small size plants.

*4.2.4. Gaseous product cleaning*

Alternative and sustainable sewage sludge valorization methods such as the gasification process should be considered in regarding to their environmental impact as well. Since Sewage sludge contains undesirable elements the syngas contains also impurities and in particular in the form of solid particles, fly-ash, inorganic compounds and condensable tar. Cleaning of the gas is of the main importance in the biomass energy systems. To this respect, technological hurdles of sewage sludge gasification in order the technology to become more economically competitive, mainly refer to scale up, tar reduction and gas cleaning [89].

Tar resulting from the pyrolysis zone is a major problem, sometimes responsible for operating failures such as equipment blocking and fouling, due to its viscous character and its tendency to condense at low temperatures. Catalysts, scrubbers (cyclones, filters) and optimum performance conditions may lead to tar reduction [90,91]. Phuphuakrat et al. [92] reports that the most important operating parameter affecting tar production during sewage sludge gasification is the amount of air supply (the equivalence ratio, ER). Higher ER remarkably reduces the total tar mass, while, focusing on tar components, increasing ER decreased yield of tar components of lower molecular weight whereas heavier tar was increased; maximum amount of tar collected at the exit of the gas cleaning system was as high as 3.3 g/m$^3$, with highest percentage of light aromatic hydrocarbon tar, which are non-condensable at the operating temperature and not harmful to engines.

Capture and removal of the ash from the gaseous product is also a matter of concern. Sewage sludge high ash content and even toxic character requires safe disposal to the downstreams of the gasifier; thus, is extensively reviewed below.

## 5. Technological aspects

The energetic valorization of sludge at industrial level covers combustion or co-incineration with other solid fuels, especially coal, for heat production. Gasification and pyrolysis of sewage sludge (with or without mixing with biomass or other waste) is still in experimental or pilot stage, although both processes are in general more efficient than combustion and allow heat and power cogeneration.

Capital and operating costs are almost similar for both pyrolysis and gasification processes [85]; the principal difference between the two processes lies in the product value and environmental impacts. The fact that gasification produces a single clean product makes it more attractive than pyrolysis for in situ installation near by the sewage-treatment plant. The dispersed nature of WWTPs also seems to favour simple small-scale sewage sludge energy production plants operated in situ at atmospheric pressure, without the cost and infrastructure complexities of using it as a co-fuel [93]. Dogru et al. [82] states that small scale gasifiers-CHP, could make an important contribution to the economy of rural areas where sewage sludge is adequately produced. Integrated gasification – fuel cell systems are preferable for relatively small scale installations, since the electrical efficiency percent exceeds 30%, for those capacity systems.

An important parameter that influences the thermal processes efficiency, when dealing with sewage sludge exploitation, is the increased moisture content. The sludge produced in WWTPs, normally, consists of ~95 wt% moisture, after solids' sedimentation by gravity. In order to reduce the moisture content dewatering and drying processes are applied. Despite the initial dewatering by filter pressing or centrifugation, the moisture content of sludge still exceeds ~70 wt%. A drying process can be also applied to achieve more than ~90 wt% water removal but consumes large amounts of energy, raising its disposal cost; thus, a crucial point in sewage sludge management is dealing with the increased moisture

content, since a wide range of relevant applications are commercially available for lower moisture feedings.

The application of an energy production process that could operate in an energy efficient-cost effective-manner, avoiding the drying of the feedstock, whereas exploiting the moisture content, appears challenging. Gasification could run with moisture content of sludge as high as ~75%, while pyrolysis' operation at medium temperatures restricts the moisture content of sewage sludge in the feedstock at the percentage of ~15%. Alternative pyrolysis of highly wet sewage sludge, at high temperatures, towards the direction of hydrogen rich fuel gas production is under discussion for its viability; the aspect is further analysed below.

In the case of using sludge as an alternative fuel in an existing power or cement plant, an adjustment of the experimental conditions, rather than major modifications in the existing installations, is most advisable [88].

Some worth mentioned applied technologies are quoted as follows:

### 5.1. Oil-from-sludge technology (OFS)

A successful pyrolysis/gasification process that enhances bio-oil production is the oil-from-sludge technology (OFS), including dried sewage sludge thermal conversion into char, oil and non condensable gases, at approximately 450 °C for more than 30 min in atmospheric pressure. The vapours are brought into contact with the char and converted into straight chain hydrocarbons, which are then condensed into oil [35]. It is also stated that sludge pyrolysis' char catalytically converts the oil from sludge (OFS) into straight chain hydrocarbons of high heating value and low viscosity, due to the catalytic effect of some heavy metals in the form of salts contained in char [39].

### 5.2. Carver-Greenfield technology (C-R)

Another example is Carver-Greenfield pyrolysis-based technology (C-R). This process results to a refuse-derived fuel (RDF) [94]. Sewage sludge is combusted or gasified, after it is simultaneously drying within the process. Specifically, raw sewage sludge is mixed with oil waste (used motor oil) and the mixture is passed through an evaporating system in order to remove the water. The dried sludge is then centrifuged to separate liquid from the solid phase. As a result a solid waste and a liquid fuel, exploited back in the installation arise [95].

### 5.3. The Lurgi–Ruhrgas gasification process

The process is based on a circulating fluidized bed reactor and leads to high conversion level and high calorific value of the product gas due to the increased contact brought about the recirculating fluidized medium. In particular, gas produced has calorific value as high as 24 MJ/m$^3$ [85].

### 5.4. The Siemens Schwell–Brenna technology

The process includes co-pyrolysis at 450 °C of a mixture of sewage sludge and crushed wastes in a rotary kiln and combustion of the residual char and gas product at ~1300 °C, using boiler for heat recovery [85,95].

### 5.5. The ChemChar waste gasification process

ChemChar process is a gasification process that maximizes carbonaceous char residues production originating from sludge and has shown promise as a means of treating and drying sludge [96]. A batch mode is commonly used for laboratory studies to simulate full scale, continuous feed operations. During the process, by repeated cycles of mixing char residue with moist sludge, drying, and gasification, all of the organic carbon in sludge is eventually converted to combustible gas and mineral residue (ash). A major advantage of the process is the retention of heavy metals on the char matrix.

Opposed to other gasification processes in which the objective normally is to convert essentially all the carbonaceous material to combustible gas, maximizing char production makes the process very useful for the treatment of sewage sludge. Char has excellent drying and conditioning abilities when is mixed with additional wet sludge that can be then gasified, thus completing a whole cycle of dewatering and gasification [81]. The gas product of sewage sludge gasification is normally approximately 50% by volume $CO_2$, and of the remainder, slightly more than half is CO, and slightly less than half is elemental $H_2$. In addition, detectable quantities of methane are usually produced.

## 6. Environmental aspects

Sewage sludge may accumulate considerable amounts of sulphur, chlorine, and especially nitrogen, together with other elements, such as heavy metals, which may lead to the release of pollutants rendering its disposal and utilization problematic.

In case of sewage sludge's exploitation for energy production through thermochemical processes, is important to ascertain their mobility as these contaminants can potentially be met in all the three products formed during thermochemical processes (gas, char, tar). Especially for atmospheric pollution, as well as gas exploitation in different pathways (engines, turbines, fuel cells, etc.) it is very important to determine the gas quality emerging from sewage sludge gasification.

According to the literature review that follows, it is expected that most of the gaseous compounds of nitrogen, sulphur, and chlorine, due to the reducing conditions used, appear as $H_2S$, $NH_3$, and HCl [88]. The presence of these compounds is undesirable for most syngas applications. Therefore, their formation should be minimized and controlled. The formation of these compounds during thermochemical conversion has been studied by several authors reported as follows [97–107].

Sewage sludge also contains variable quantities of other elements, including heavy metals, as previously analysed. These elements may be volatilized to the gas phase at high temperature, or they may be retained by the solid bed residue, trapping some of the nitrogen, sulphur, and chlorine introduced by the feedstock [88,108,109]. Thermodynamic equilibrium modelling is used to explain the observed behaviour in the many of the reviewed studies.

The typical metal concentrations in sewage sludge are shown in Table 6 [13,110]. Principal contaminants present in sewage sludge are zinc (Zn), copper (Cu), nickel (Ni), cadmium (Cd), lead (Pb), mercury (Hg) and chromium (Cr).

Trace elements specific chemical forms and binding patterns determine their mobility and ecotoxicity [111–114]. Therefore, it is, obviously crucial to trace the evolution of chemical forms of heavy metals throughout the sludge treatment applying speciation techniques in order to obtain meaningful data on both bioavailability and toxicity and suggest their potential disposal options [115,116].

During recent decades, many scientific methods [110,114,116–119] assess qualitatively and quantitatively the bioavailable metal fraction and the potential mobility of trace metals in sludge, soils and sediments. However, none of the performed extraction schemes has been unreservedly accepted by the scientific community [117,118]. The results obtained are difficult

**Table 6**
Typical metal content in wastewater sludge [13,110].

| Metal | Dry sludge (mg/kg) | |
|---|---|---|
| | Range | Median |
| Arsenic | 1.1–230 | 10 |
| Cadmium | 1–3.410 | 10 |
| Chromium | 10–990,000 | 500 |
| Cobalt | 11.3–2490 | 30 |
| Copper | 84–17,000 | 800 |
| Iron | 1000–154,000 | 17,000 |
| Lead | 13–26,000 | 500 |
| Manganese | 32–9870 | 260 |
| Mercury | 0.6–56 | 6 |
| Molybdenum | 0.1–214 | 4 |
| Nickel | 2–5300 | 80 |
| Selenium | 1.7–17.2 | 5 |
| Tin | 2.6–329 | 14 |
| Zinc | 101–49,000 | 1700 |

to compare, since they depend on the original effluent's load and its subsequent treatment and furthermore, on the extraction method performed [119–122]. The Community Bureau of Reference (BCR) in order to harmonize the methodology used in sequential extraction schemes for the determination of extractable trace metals in soils and sediments indicates a sequential extraction analysis procedure [123], which has been successfully applied in various matrices, including sewage sludge [116,124,125].

A basic insight into the nitrogen, sulphur, chlorine transformations and heavy metals mobility is crucial for clean utilization of sludge as an energy source.

### 6.1. Fate of N-containing compounds

Nitrogen transformations during thermochemical conversion have been studied. According to Cao et al. [97] $NH_3$ was found to be the predominant nitrogenous gas under all the fast pyrolysis operating conditions. Raising temperature and decreasing sweeping gas flow rate leads to increasing yields. High protein content in the sludge is responsible for significant $NH_3$ at temperatures lower than 500 °C. HCN was lower than 2% during pyrolysis below 550 °C, and sharply increased to 5.8% at 700 °C due to thermal cracking of volatile matter. Water-insoluble nitrogen-and carbon-containing species were significantly decomposed to water-soluble ones during secondary reactions. At high temperatures, heavy hydrocarbons were mainly cracked to gaseous products, while the nitrogen-containing species tended to form water-soluble species. Thermal cracking of volatiles is the main route for HCN formation, while $NH_3$ production at temperatures lowers than 400–500 °C is due to aminostructures in sewage sludge and at higher temperatures due to hydrogenation of N-containing structures in the pyrolysing solid particles.

Furthermore, attempting to investigate the nitrogen transformation into $NH_3$ and $N_2$ Drift et al. [99] used a circulating fluidized-bed gasifier and various biomass fuels as feedstock and concluded that the concentration of $NH_3$ in the product gas depended upon the amount of nitrogen present in the fuel; thus, about 60% of the fuel-bound nitrogen was converted to $NH_3$. In the same direction Zhou et al. [100] notices that most of the fuel nitrogen is released as $NH_3$ and $N_2$, while less than 1% of the nitrogen in the feedstock is detected as HCN and NO.

Finally, under the ChemChar waste handling process Medcalf and Manahan [101] states that elemental nitrogen is evolved as elemental nitrogen gas, while $NH_3$ and some HCN also appear under some conditions.

Especially $NH_3$ formation and destruction during sewage sludge gasification depends on several parameters, such as gasification temperature, steam and oxygen contents in the gasification medium, fuels' nitrogen content, and even inorganic matter presence at the feedstock or the reactor's material, as they may interact in $NH_3$ formation reactions [102,103]. Specifically, decomposition of $NH_3$ is an endothermic reaction favoured by temperature increase. Additionally, oxygen increase also decreases $NH_3$ release as it leads to increase in the formation of NO, which decomposes to $N_2$ under the reducing conditions of gasification; therefore, less $NH_3$ would be formed.

### 6.2. Fate of S-compounds

High sulphur content in sewage sludge results in $H_2S$ formation in the gas product. Karayildirim et al. [57] determined the amount of hydrogen sulphide in the pyrolytic gas around ~2 wt%, and explained that in case of mixed and oil sludge that chose to use for their experiments are evolved due to degradation of bacteria or organic sulphur compounds such as mercaptanes, thiophenes, respectively. Kuramochi et al. [104] measured $H_2S$ contents of around 0.4 vol% in the gasification gas, due to high sulphur levels in sewage sludge.

Medcalf et al. [105] states that elemental sulphur is deposited on the char and $H_2S$ released in the gas product under the ChemChar process, and indicates the method for the destruction of sulphur containing waste.

Sulphur reaction with the feedstock inorganic matter, such as Fe and Ca, causes its retention in the char [104]. Khan [106] showed that the form in which sulphur was present in sewage sludge; either in organic or inorganic compounds determined its distribution between the different fractions (char, tars, and the fuel gas). The same authors noticed the effect of temperature and oxygen flow rate on the $H_2S$ formation; higher temperatures increased the $H_2S$ formation and release in the gas phase, while, raise of oxygen flow rate lead to $H_2S$ reduction, probably due to the formation of more $SO_2$ from fuel-S when oxygen rate was increased.

### 6.3. Cl-compounds transformation

C–Cl bonds in organochlorine compounds are classified among the most common and hazardous waste constituents [81]. Atomic H is a reactive intermediate produced during the gasification process; additionally, a powerful reductant, able to break strong C–Cl bonds.

Chlorine form, organic or inorganic has been reported by Li et al. [107] coal pyrolysis studies to be responsible for chlorine mobilization to the gas phase. Temperature increase leads to higher chlorine release in the gaseous phase, regardless of chlorine form. Towards the same direction Kuramochi et al. [104] also stated the dependence of HCl release on temperature and indicated the influence of the presence of elements, such as K, Al, Na, and Si, and the competition among them to react with chlorine. Other elements, such as Si, Al, and Ca, and heavy metals, may retain chlorine; thus determine HCl formation and release [104].

### 6.4. Heavy metals' mobility towards products

Sewage sludge is considered to be under scrutiny for its high metal content. Zn, Pb, Cu, Cr, Ni, Cd and Hg concentrations in sludge vary from less than 1 ppm to more than 1000 ppm and potentially cause ecotoxicological risks [126]. Regarding, other feedstock used as carbon sources in energy production, the mobility and fate of heavy metals are a matter of concern, including sewage sludge.

In terms of sewage sludge thermochemical conversion via pyrolysis and gasification, trace elements mostly appear at the char residue or gas product. Considerable amounts are also present in the liquid pyrolysis' products, as was stated above. Trace elements could mobile to the gas phase either as vapours or aerosols. The volatilization of trace elements is mostly related to their boiling

point; thus, gasification high operation temperatures opposed to pyrolysis results to an increased risk of gaseous product contamination and hence the importance of monitoring the metal distribution during the gasification process. Analysis that follows demonstrates the possible pathways of heavy metals to the various process products. The potential implications of these findings for process design, operating conditions, and residue disposal are discussed.

Stammbach et al. [30] studied pyrolysis of sewage sludge in a fluidized bed reactor in the temperature range 500–650 °C and reported that the heavy metals, Cu, Cr, Pb, and Zn are not vapourized under the experimental conditions, whereas, are enriched in the solid residues. The emission of these metals as particles depends on gas/solid separation. The process is complete under the conditions of a fluidized bed above the temperature of 600 °C, while Cd's emission out of the solid residues begins at 560 °C; thus it is obviously stated that pyrolysis should be limited to temperatures not much higher than 600 °C. An economically acceptable method to restrict Hg emission is concluded to be necessary.

He et al. [127] in their pyrolysis study focused on the potential bioavailability of Cu, Zn, Pb and Cd in sewage sludge and in the pyrolysis residues and evaluate the effect of pyrolysis temperature on the speciation distribution of these metals in the residues. The research concludes that Cd is volatilized to the off-gas when the temperature rises to 700 °C, appearing a sharp decrease in the solid residue. Furthermore, Cu, Pb and Cd, in the sludge and the residues, are mainly bound to organic matter and sulphides, while Zn is mainly bound to Fe and Mn oxides. In addition, results noticed that the temperature does not effectively contribute to the distribution of metal speciation in the residues till it reaches a certain value. This study aiming to identify the relationship between the leaching behaviour of these metals in the residues and pyrolysis temperature shows that pyrolysis enhances the stability of these four metals when the temperatures rise up to certain values.

In considering the fate of potentially harmful heavy metals during gasification process, it should be noted that ash dust is the major carrier of heavy metals including Cd and Pb in turbulent waste gasification processes; thus, if the process operates under non turbulent conditions, particulate ash emissions are virtually eliminated [128].

According to Saveyn et al. [129] heavy metals' distribution following sewage sludge gasification, indicated that metals such as Cu, Pb, Zn mainly retrieved in the char, while, Hg and Cd are depleted from the sewage sludge and end up in the different downstream parts (char residues, condensate liquids, particles trapped in filters). It is reported that the point at which the major losses occur is clearly related to the boiling point of the different metals, being 357 °C for Hg and 765 °C for Cd at atmospheric pressure. Bool and Helble [130] work on gasification of coal and lead to similar findings.

Marrero et al. [81] studied the behaviour of selected heavy metals injected to sewage sludge – Cd, Cs, Co, As, Hg, Zn and Cu – during the ChemChar gasification process. They reported the strong metals tendency to remain on the char. Additionally, Colbert et al. [131] and Martin et al. [132] noticed that heavy metals may be retained in the condensate and on the char filter leading to generally complete retention of metals within the total gasification system. Colbert et al. [131] indicated that significant fractions of Hg were mobilized from the gasifier, however, this volatile element was retained within the system. It was also revealed that there is a strong possibility of all of the Hg to be mobilized with aerosol particles. This points out the necessity to reduce aerosol formation and increase collection in the gasification process. Additionally, a significant quantity of aerosol was produced and some volatile elements (As) were likely to partially enter the vapour state and condense with aerosol particles to be carried from the gasifier. Especially under the reducing conditions of gasification, As may have been partially converted to $AsH_3$.

In general [81], as far as it concerns the fate of heavy metals and their mobility to the gaseous fraction, the most important conclusions were the followings:

- Arsenic is mobilized in a small but measurable extent. 1 wt% of As is detected in the effluent gas.
- Although mercury is the most mobile metal, it retained in the char filter formed from the gasification of the sludge. An aerosol product of the process is responsible for the mobility of mercury to gas stream.
- Reed et al. [93] investigated the effect of the gasifier bed temperature (770–960 °C) and the type of sewage sludge and came to the following conclusions.
- Under all of the conditions studied, no mercury retention in the solid residues was observed.
- Cobalt, copper, manganese, and vanadium were neither depleted from the bed residue nor enriched in the fines.
- The extent of barium, lead, and zinc depletion from the bed residue varies with sludge type, and the enrichment of lead in the fines seems to be enhanced by gasifier bed temperatures in excess of 900 °C.

During gasification, attrition, entrainment, and volatilization attribute to the release of trace elements from the feed. The process could be described as follows [93]; trace elements enter the gas phase and may, in turn, be condensed into solid or liquid aerosol, by a combination of chemical reaction, homogeneous and heterogeneous condensation, and absorption mechanisms, as the gases cool after leaving the gasifier bed. The extent to which trace elements are depleted from the bed char, condense on the gasifier fines and removed from the product gas by the gas-cleaning system may be element-specific.

Generally, the extent to which this constitutes becomes an emission problem is dependent on the effectiveness of the gas-cleaning system. The observed behaviour of these elements is discussed in relation to their speciation, as predicted by thermodynamic equilibrium modelling [93].

## 7. New thinking in sewage sludge treatment and disposal

Towards the direction of dealing with the intensified sewage sludge treatment and disposal problem appears the need for innovative, scientific techniques, combined methodologies and out-of-the box thinking; thus, are discussed the following issues.

### *7.1. $H_2$ production from wet sewage sludge*

The prospect of producing hydrogen-rich fuel gas, subjecting wet sewage sludge to thermochemical treatments that combine drying, pyrolysis and gasification, has been investigated in several studies [26,49,53,64,83,133], suggesting that the presence of moisture is favourable for the generation of $H_2$; thus, wet sewage sludge can be assumed as one of the most common feedstock to hydrogen gas manufacture all over the world [82].

Wet sewage sludge pyrolysis at high temperatures combined with high heating rates enhances the production of $H_2$-rich fuel gas [53,64]. It was found that subjecting vapours formed during pyrolysis of wet sludge to long residence times and high heating rates at $T \sim 1000$ °C, results in higher gaseous product fraction. Moreover a gaseous product of much higher $H_2$ percentage is produced from pyrolysis of wet sludge rather than dry. The high moisture content [49] of sewage sludge generates, at high temperatures, a steam-rich atmosphere, leading consequently to an in situ steam reforming of the volatile compounds and to a partial gasification of the solid char, which contributes to the production of hydrogen-rich fuel gas.

Additionally, microwave pyrolysis of wet sewage sludge compared to conventional carried out under the most similar conditions, leads to lower non-condensable gas production, with a high content of CO and $H_2$ (synthesis gas), while conventional in an electrical furnace to gas generation with high content of light hydrocarbons. Wet sewage sludge is in both cases, efficiently dried and pyrolysed [26,133]. Life Cycle Analysis is needed in order to scale-up and assess the sustainability of the recommended process. In any case the pyrolysis results are indicative for the expected ones during gasification. Furthermore, sewage sludge moisture content investigation on air gasification indicates that increased humidity in the feedstock is beneficial to the process results [83]. Specifically, the quality of the gas product improves by increasing moisture content in sludge. $CO_2$, $CH_4$, and $H_2$ concentration, low heating value of the produced gas ($LHV_{gas}$) and aqueous yield increase by increasing moisture content, while CO concentration and tar yield decrease. Of course steam reforming reactions could be further enhanced using appropriate catalyst and niche efficient technologies.

### 7.2. Co-pyrolysis and co-gasification of sewage sludge with biomass

The utilization of sewage sludge blends with biomass residues, as a feedstock in the thermochemical processes of pyrolysis and gasification, seems to be an interesting prospect, in order to improve of the alternative fuel's characteristics. In general such a practice may result in moisture reduction of sludge, increase of calorific value and dilution of the sludge's undesirable species content.

Sewage sludge has some special physicochemical characteristics, such as high moisture content, high ash content, low heating value, density and viscosity. Crop biomass contains, comparatively to sewage sludge, less ash, and in general has low energy density and low ash melting point (ash fusion temperature) [134,135] though, it can be transformed into high heating value thermochemical products. Mixing the two materials, in an appropriate proportion, may compensate both residues weaknesses and the new blend-material may have improved mechanical and physicochemical characteristics; thus some studies has been performed concerning co-pyrolysis and co-gasification of, e.g., biomass-coal [136], as well as sludge-coal [137,138]. However, research on the co-pyrolysis and co-gasification of sludge–biomass mixtures has been shortly reported yet.

Folgueras et al. [98] studied pyrolysis of coal blended with sewage sludge and showed that sludge is more reactive than coal. Its decomposition and devolatilization took place at lower temperatures. Moreover, Pinto et al. [109] reported that the addition of sewage sludge during coal gasification increased the calorific value of the fuel gas, as well as the fuel conversion. Zhang et al. [139] studied the co-pyrolysis behaviour of dried sewage sludge and crop biomass mixtures through TG. Rice straw, which was regionally abundant, was mixed with sludge and was found that this straw significantly affected the release of volatile matter in the co-pyrolysis process. It was also observed that the volatile matter was more sufficient and the weight loss and weight loss rate increased with the increase of the rice straw percentage in the blend.

The effect of the addition of biomass (straw pellets) in dried sewage sludge was also reported at Pinto's et al. [88] work concerning biomass–sludge co-gasification. They concluded that the presence of biomass had a positive effect in the syngas production. Sewage sludge enhanced the hydrocarbon content in the gaseous product, and as straw pellets presented higher content of volatiles that released fast, cracking and reforming reactions of these compounds led to lower hydrocarbons content.

Kinetic analysis of the co-process demonstrates that synergistic or coupling effects accelerate the release of volatile matter [139]. It is concluded that the co-pyrolysis' kinetic parameters are not conducted just from a simple summation calculation, but using the experimental information data. The parameters in the stage of volatile matter liberation, which can be well linear, fitted, and described at a satisfactory level by a first order reaction, together with Arrhenius low, have kinetic compensation effect in the process of co-pyrolysis.

An integrated approach is most advisable, considering the environmental implications of the process. As mentioned above, sewage sludge usually contains large amounts of S-, N- and Cl-compounds, while, heavy metals are also present in its composition at variable quantities. Co-processing takes benefit of the biomass diluting effect on the sludge's undesirable species. Co-gasification of sewage sludge blended with biomass leads to lower concentrations of both $NH_3$ and $H_2S$ in the gas product, due to the low nitrogen and especially sulphur content of straw pellets [88]. High HCl content in the gas is relevant to its presence in the feedstock; thus $NH_3$ and HCl contents in gasification gas, after a condensation system, are very low.

### 7.3. The prospect of wastewater-grown algal thermal processing

Among other biomass species algae are a potential source of renewable energy. Microalgae can generate lipids sometimes at significant concentrations, while, they, also, present high productivity. It is estimated [140] that bio-fuel production from algae is potentially, both economically and environmentally sustainable. However, further optimization of mass culture conditions is needed in order to have a total positive energy return [141]; Wastewater-grown microalgae have been reported high biomass productivities and, also, in some cases high lipid productivities suggesting the real potential in the utilization of these high nutrient resources for economically viable and sustainable bio-fuel production.

Algal cultivated in wastewaters derived from municipal, agricultural and industrial activities, and then used for fuel and energy production could potentially provide cost-effective and sustainable alternative renewable energy source [142].

The algal bio-fuel production using wastewater resources has been thoroughly reviewed by Pittman et al. [141]. Combining wastewater treatment, such as nutrient, chemical, organic contaminants, heavy metals and pathogens removal, by algae cultivation, with bio-fuel production has been argued to be the field with the most plausible commercial application in the short term [143]. In particular, co-processing biofuel production, wastewater treatment and fertilizer recycling is seen as a near-term application (5–10 years), since the algae are already used in wastewater treatment [144,145].

Limitations that need to be addressed concern the following [141]:

- Efficient algae harvesting techniques. Efficient and costly harvesting is the major problem for the sustainability of this application.
- High biomass and lipid productivity at pond scale.
- The need for life cycle analysis of waste-water derived algal biofuel.

Microalgae biomass can be processed and converted to biofuel by a variety of methods. Since microalgae have high moisture content, biomass energy conversion processes are limited [142]. Thermochemical processes result in bio-oil and bio-gas production, while biochemical processes lead to ethanol and biodiesel production. Lipid extraction [141] from microalgae and the use of microalgae as an oil source for biodiesel production is likely to be one of the most attractive options, particularly if the remaining residual algal biomass can be also utilized for biogas production [143].

Thermochemical conversion of algae is discussed in this work, having a further insight on pyrolysis and gasification. Pyrolysis has received special attention for generating biofuels from microalgae. Pyrolysis of algal biomass has given promising results and have been shown to produce higher quality bio-oil than lignocellulosic compounds [143]. Lipid containing biomass has been shown to produce higher heat balances and bio-oil yields [146]. Gasification of microalgae biomass has been studied by several researchers. It is estimated that algae biomass gasification at 1000 °C produced the highest theoretical yield with an estimated energy balance [147], which gives gasification a marginal positive energy balance; the low value being attributed to the use of an energy intensive centrifuge process during biomass harvesting.

Reliable literature data for the gasification of microalgae is very sparse. This area needs more research especially related to the energy balance of drying the biomass for gasification. Elliot and Sealock [148] developed a catalytic gasification process at low temperature that exploits the moisture content in the direction of high syngas production.

An integrated exploitation of the produced material of wastewater-grown microalgae via thermal processes of pyrolysis and especially gasification seems to have great potential, especially for hydrogen rich fuel gas. The increase of the lipid content of the mixture and the moisture exploitation of the blend through niche thermochemical processes are some of the advantages of the specific blend. Additionally, combined heat and power systems contribute in the energy balance of the drying process.

## 8. Conclusions

The conclusions of the present review study can be summarized as follows:

- The amount of sewage sludge produced is increasingly growing, demanding management in compliance with the law. Regulations, environmental issues, best practices with BAT (best available technologies) and cost, will determine the choices of sewage sludge disposal routes.
- Thermal processes for bio-fuels production from sewage sludge seem to have great potential, especially when considering uses of sludge as alternative fuels in existing plants and co-processing with biomass.
- Sewage sludge is highly heterogeneous and comprises a mixture of various organic and inorganic compounds. It also contains variable quantities of other elements, including heavy metals. During thermal conversion, and especially gasification most of the gaseous compounds of nitrogen, sulphur, and chlorine, appear as $H_2S$, $NH_3$, and HCl due to the reducing conditions used. In case of sludge exploitation for energy production through thermochemical processes, it is important to ascertain the mobility of these contaminants as they can potentially be met in all the three products formed (gas, char, tar).
- Since sewage sludge contains undesirable elements the syngas also contains impurities and in particular in the form of solid particles, fly-ash, inorganic compounds and condensable tar. The presence of these compounds is undesirable for most syngas applications. Therefore, their formation should be minimized and controlled. Especially for the use of the producer gas in different pathways (engines, turbines, fuel cells, etc.), it is very important to determine the gas quality by cleaning in order to assure good operation.
- Some sewage sludge problematic characteristics, such as high moisture content, inorganic elements, and toxic compounds, could be over passed through co-processing with biomass because in that way reduction of the above characteristics can be obtained.
- Sewage sludge moisture content investigation on gasification and pyrolysis at high temperature indicates that increased humidity in the feedstock could not be a barrier at a certain extent but rather beneficial to the process results especially for $H_2$ rich gas product with the development of niche efficient technologies and appropriate catalysts. Furthermore, combined heat and power systems contribute in the energy balance of the drying process.
- There are technological barriers in the large scale application of thermochemical processes. In order to overcome the technological limits in sewage sludge gasification and to develop a more economically competitive technology as well as environmentally sound, process scale up, tar reduction and gas cleaning are subject being under research, investigation and study.
- The innovation on sewage sludge management lays in the modern thinking that microalgae cultivation in sludge could offer phyto-remediation in municipal wastewater plants and by further exploitation of the biomass produced bio-fuel and $H_2$ rich gas production.
- Therefore, the prospect of thermochemical exploitation of such a material (algae in sewage sludge) is under research and study.

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